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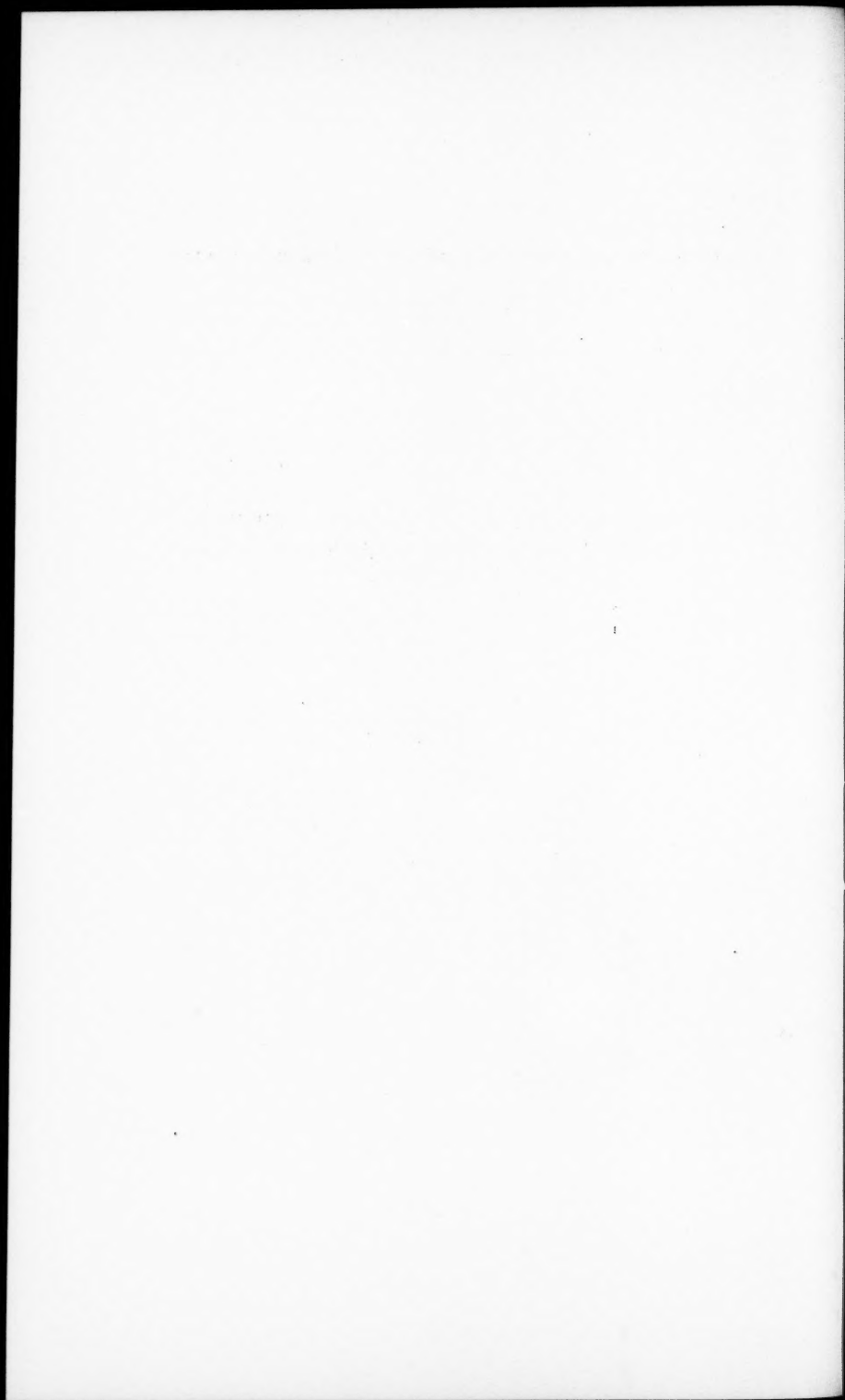
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THE COMPRESSIBILITY AND PRESSURE COEFFICIENT  
OF RESISTANCE OF SEVERAL ELEMENTS AND  
SINGLE CRYSTALS.

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## INTRODUCTION.

This paper is in continuation of my program of determining the quantities indicated in the title for all the well defined materials possible, particularly elements and single crystals.<sup>1</sup> The novel feature in this paper is that there are included measurements of the linear compressibility in different directions of single crystals of several organic substances, a class of substance for which these measurements have not hitherto been made. This has demanded the construction of a new type of piezometer, the former type not

being applicable because in it pressure is transmitted directly to the specimen by kerosene, in which most organic substances dissolve.

#### APPARATUS AND METHOD.

The design of the new piezometer is indicated in Figure 1. The specimen is submerged in mercury, by which pressure is transmitted to it. The specimen under pressure is connected to a manganin

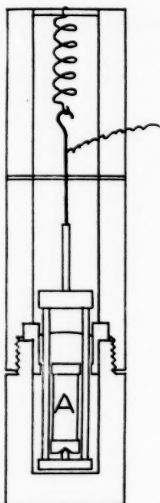


FIGURE 1. Diagram of the new form of piezometer, in which the specimen, A, is submerged under mercury to prevent action between the kerosene by which pressure is transmitted and the specimen.

wire, held pressed tightly against it by a spring, the wire sliding over a fixed contact, so that the change of dimensions of the specimen under pressure can be determined in terms of resistance measurements on a potentiometer, exactly as in the previous types of piezometer. Corrections must be applied to the readings, similar in character to the corrections demanded by the other forms of piezometer, for the linear compressibility of the steel parts, the linear compressibility of the manganin wire, and the change of specific

resistance of the manganin under pressure. These corrections have been determined by direct and indirect measurement. In addition to these corrections which can be calculated, there are other corrections arising from small effects which cannot be determined so easily, such for example, as that arising from the compressibility of the insulating washers of mica, or from internal strains in the metal parts at the various screw connections. These corrections were determined together by measuring with the apparatus the compressibility of pure iron, the compressibility of which is already known, and finding the corrections which must be added to the calculated corrections to give the known compressibility. These corrections altogether amounted to a change of length of about 0.002 cm at 10000 kg/cm<sup>2</sup>.

It will be noticed that in this apparatus the changes of dimensions are measured directly, without multiplication as in the previous piezometer. The necessity for this arose from the fact that many organic substances are too weak mechanically to withstand the stress to which they must be subjected in the multiplying apparatus. In using the piezometer, small specimens had to be measured in a number of cases, because it is often difficult to obtain crystals of organic substances of any size. In consequence of these two facts, the measured effects were often small, and the corrections were sometimes as much as 50% of the measured effect. The accuracy with this type of apparatus is not as high as that obtainable with the previous types, which still are to be used whenever the substance will allow it.

There follows now the detailed description of the various measurements.

#### EFFECT OF PRESSURE ON ELECTRICAL RESISTANCE.

*Indium.* This material was of exceptionally high purity, having been made by Professor T. W. Richards in connection with determinations of its atomic weight. I owe my supply to the kindness of Dr. L. H. Hall, to whom was intrusted the task of winding up many of the scientific affairs of Professor Richards after his death.

The potentiometer method of measurement was used. The wire, of about 0.035 cm diameter, was made by cold extrusion through steel dies. The piece measured was about 10 cm. long, bent into a hair pin shape. The terminals were fine wires of pure silver, fused directly to the indium by a simply constructed arrangement utilizing

the Joulean heating of a current through the silver. The use of solder in attaching the terminals was undesirable because indium forms with tin and lead an alloy of melting point lower than  $75^{\circ}$ , at which it was desired to make measurements.

Measurements of the effect of pressure on resistance were made in the regular way up to 12000 kg at  $30^{\circ}$  and  $75^{\circ}$ . The pressure measurements went very smoothly; the mean departure of a single point from a smooth curve at  $30^{\circ}$  being 0.09% of the maximum effect, and at  $75^{\circ}$  0.03%. The relation between change of resistance and pressure is very nearly of the second degree, but departs from it

TABLE I.  
THE RESISTANCE OF INDIUM UNDER PRESSURE.

Pressure Kg/cm <sup>2</sup>	$-\frac{\Delta R}{R(0, 30^{\circ})}$	$-\frac{\Delta R}{R(0.75^{\circ})}$
2000	.0288	.0302
4000	.0549	.0575
6000	.0795	.0831
8000	.1026	.1075
10000	.1245	.1295
12000	.1450	.1504

by more than the experimental error, the pressure of maximum departure from linearity being somewhat less than the mean pressure. The accompanying table gives the effect at pressure intervals of 2000 kg. The initial resistances at atmospheric pressure at  $30^{\circ}$  and  $75^{\circ}$  were 1.1472 and 1.3678 respectively, in terms of the resistance at  $0^{\circ}$ .

The temperature coefficient of resistance at atmospheric pressure between  $0^{\circ}$  and  $100^{\circ}$ , obtained by linear extrapolation of actual readings at  $25^{\circ}$  and  $75^{\circ}$ , was 0.004904. By combining with the values in the table for the effect of pressure, the corresponding temperature coefficient at 12000 is found to be 0.004876, thus agreeing with the result found for many other metals that the temperature coefficient is little affected by pressure.

I have previously measured the effect of pressure on the resistance of a sample of indium of inferior purity.<sup>2</sup> The mean coefficient to 12000 of the pure metal is about 15% greater than that of the former sample, agreeing with the universal rule that the coefficient of the purer metal is less algebraically than that of its alloys. The temperature coefficient of the former sample was 0.00404, against the

value 0.00490 for this new pure material. The new value is higher than any listed value of the temperature coefficient.

*Manganese.* This material I owe to the kindness of Professor M. A. Hunter of Rensselaer Polytechnic Institute, who prepared it in massive form by electrolysis of the fused salts. The specimen on which the resistance measurements were made was in the form of wire several cm long and of the order of 0.5 mm in diameter. It was most kindly prepared from the massive material by Mr. G. F. Taylor of the General Electric Co. at Schenectady by his method of drawing out a tube of glass or quartz containing the metal heated above its melting point.

Manganese is a metal which previous investigators have found very difficult to get into massive form without the formation of numerous cracks which destroy the continuity of the metal. These cracks have been attributed to a polymorphic transition which manganese passes through on cooling from the melting point to room temperature. The transition is accompanied by a large change of volume. It would be expected that this difficulty would make impossible the formation of wire by the Taylor process. Doubtless the effect was present, for although the quartz capillaries in which the manganese was drawn out were 10 or 15 cm long, and they were apparently completely filled with a thread of manganese, the thread always broke into lengths varying from a few millimeters to one or two centimeters. These short lengths were very strong mechanically, being very difficult to break with the fingers, and not showing any of the brittleness usually associated with metallic manganese. The places in which the thread broke doubtless corresponded to the cracks usually found in the massive metal. It is possible that the coherent pieces may have been single crystals of the low temperature modification.

Measurements of resistance were made by the potentiometer method. Four terminals were attached to the specimen by springs. It was not until after the completion of the measurements that I was informed by Mr. Taylor, and verified for myself, that it is very easy to solder manganese with soft solder; if I had known this in time, I would have soldered the connections, instead of using springs, because of the greater convenience.

Before making the pressure measurements, the temperature coefficient of resistance was determined at atmospheric pressure. The mean coefficient between 0° and 100°, obtained by linear extrapolation

of measurements at 25° and 75°, was 0.00078. There seem to be no published values of this coefficient, but 0.00079 is so much lower than the value customary for a pure metal that there can be little doubt that the metal contains several per cent of impurity. It is perhaps more probable that the impurity was in the original material than that it was given to it during the process of formation into wire.

In view of the probable impurity, the effect of pressure was measured only at 30°, up to 12000. The points lay smoothly, the average deviation of a single reading from a smooth curve being 0.1%. The relation between change of resistance and pressure can be represented within experimental error by a second degree formula:

$$\Delta R/R_0 = -7.012 \times 10^{-6}p + 5.63 \times 10^{-11}p^2.$$

It is thus seen that the resistance decreases with increasing pressure, as is normal, and the curvature is also in the normal direction. Perfectly pure manganese, in accordance with the universal rule, may be expected to have a negative coefficient somewhat larger numerically than the value above.

*Chromium.* The material was obtained from Eimer and Amend. It had been made by the Goldschmidt process, was quite brittle, and probably had several per cent of impurity. It was very kindly made into wire for the pressure measurements by Mr. Taylor by his method. More difficulty was experienced with this than with manganese, the particular difficulty being sticking of the metal to the quartz tube in which it was drawn out. Removal of the quartz with hydro-fluoric acid was not as successful as with some other metals, and the method finally used was mechanical, breaking away as much of the quartz as possible, and removing the remainder by rubbing with emery paper. The dimensions were about the same as for manganese. There is not the difficulty with chromium from a polymorphic transition that there is with manganese, but its greater brittleness makes the manipulation more difficult.

The potentiometer method of measurement was used. It is not possible to solder chromium with either soft solder or silver or gold. The four terminals were fine platinum wires attached by spot welding; I am much indebted to Dr. H. G. deLászló of the Mass. Inst. of Technology for very skillfully doing this.

At atmospheric pressure the temperature coefficient of resistance between 0° and 100° was found to be 0.000033. This is very low indeed, and indicates high probable impurity. The specific re-

sistance at  $30^{\circ}$  was  $160 \times 10^{-6}$ , very high, and also suggestive of impurity.

At  $30^{\circ}$ , resistance decreases linearly with pressure up to 12000, the pressure coefficient being  $-5.8 \times 10^{-7}$ . This is very small, but of the normal sign. The pure metal may also be expected to have the same negative sign, but to be considerably larger numerically. Considering the smallness of the effect, the readings were very regular, the average deviation of a single reading from a straight line corresponding to 0.12 mm on the slide wire of the potentiometer; this is equivalent to 1.7% of the maximum change of resistance.

*Arsenic.* See the next section for a description of the effect of pressure on the electrical resistance.

#### COMPRESSIBILITY.

*Arsenic.* Since the measurements of resistance under pressure and of compressibility of this element were closely related, it is best to describe them together. These results are to be regarded only as preliminary; it is evident that arsenic is highly crystalline in its properties, and the final study must be made on single crystals.

The material was from Kahlbaum, grade "K." The compressibility was determined first. I tried to make a single crystal by sealing the arsenic in a heavy quartz capillary of about 2 mm inside diameter, and slowly lowering from an electric furnace maintained above the temperature of the triple point. This attempt to make a single crystal was not successful, but nevertheless the resulting material was highly crystalline in appearance, and there was a strongly marked preferred direction of orientation. The appearance was much like that which I have often found in trying to make single crystals of tellurium by slow cooling; the cleavage planes are usually parallel to the axis of the rod, but the orientation about the axis is at random. In the case of tellurium, more rapid cooling and higher purity in the original material brings the desired result. It is possible that the arsenic may have been contaminated by the quartz during this attempt, since the inside of the capillary was somewhat pitted after the run, which lasted for 15 hours.

The compressibility of this approximately single grain was measured in the regular way with the lever piezometer for short specimens. Two runs were made to 12000 at  $30^{\circ}$ . The results of the first run were much more irregular than usual, and showed the highly unusual feature of an abnormal curvature, that is, a compressibility increasing

with increasing pressure. The second run, made more carefully, showed that the abnormal curvature was illusory; the curve really consists of two parts with a discontinuity between 6000 and 8000 kg, the slope of the low pressure branch being less than that of the high pressure branch. The explanation clearly is a polymorphic transition. It is an unusual feature of this transition that the points corresponding to the low pressure modification could be repeated after the excursion into the domain of the high pressure modification, indicating that the low pressure modification recovers its original orientation. The high pressure modification is therefore probably not formed by the chance occurrence of a nucleus and growth from it at random, but there is some definite relation between the lattices of the two modifications such as is shown, for example, by quartz.

The initial linear compressibility of the low pressure modification was  $2.2 \times 10^{-7}$ , giving for the volume compressibility  $6.6 \times 10^{-7}$  on the assumption of equal compressibility in all directions. The volume compressibility of arsenic at low pressures has been directly determined by Richards<sup>3</sup> to be  $4.4 \times 10^{-6}$ . This great discrepancy cannot possibly be due to experimental error, but must mean that the compressibility of a single arsenic crystal is very different in different directions.

The linear compressibility of the high pressure modification was  $2.3 \times 10^{-7}$ , slightly higher than that of the low pressure modification, but the exact significance of this result cannot be clear until the relative orientation of the two phases is known.

In order to investigate more accurately the transition phenomena, the resistance under pressure of arsenic was measured. For the resistance measurements the arsenic was cast in quartz in the form of a rod several centimeters long and about 1 mm in diameter. The procedure in making the casting was so much like that described by Kapitza<sup>4</sup> in a paper published after this work was done that it is not necessary for me to add anything in the way of description. I also observed the fluorescence of the arsenic vapor in the tube, but I would describe the color as greenish yellow rather than as reddish yellow. My rod was not a single crystal grain like that of Kapitza. The production of the casting required only a few minutes, instead of many hours as before, and there was no pitting of the inside of the quartz capillary. The high purity of this arsenic was verified by measuring its temperature coefficient of resistance at atmospheric pressure. The mean coefficient between 0° and 100°, obtained by

linear extrapolation of readings at 30° and 75°, was found to be 0.00474 immediately before the casting had been subjected to pressure, and 0.00472 after several exposures to pressure and the consequent formation of the high pressure modification. This is considerably higher than any listed value for the temperature coefficient.

The pressure measurements of resistance were made in the regular way with the potentiometer; the leads were fine silver wire attached with soft solder. Special pains was taken to get the initial effect on the virgin specimen at low pressures before the transition had occurred. Points were thus obtained on a smooth curve, the resistance *increasing* with increasing pressure. A discontinuity occurred with increase of pressure between 5050 and 6030 kg. The accidental breaking of one of the connections at the maximum pressure prevented measurements of the change of resistance with decreasing pressure. On the next application of pressure the effect on the low pressure modification had changed sign, the resistance now decreasing, with the coefficient  $-1.52 \times 10^{-6}$ . A discontinuity was again found with increase of resistance, this time in the neighborhood of 5500 kg. On decreasing pressure an enormous hysteresis was found in the resistance of the high pressure modification, but the discontinuity was at essentially the same place as before, and the pressure coefficient of the low pressure modification was not much altered.

A second piece of arsenic was tried. Trouble with the connections made it impossible to get readings on the virgin specimen. The second application of pressure gave a pressure coefficient of resistance of  $-1.58 \times 10^{-6}$  for the low pressure modification, and a discontinuity between 5400 and 5800. The behavior on releasing pressure was approximately the same as before; very great hysteresis in the resistance of the high pressure modification, and a discontinuity, now a little more pronounced than before, at approximately the same pressure, and again approximately the same pressure coefficient for the low pressure modification.

The best value for the transition pressure from the resistance measurements is 5500 kg, somewhat lower than the lower limit found from the compressibility measurements.

These results obtained with arsenic may be summarized as follows. There is a new modification at high pressures, and the transition pressure at 30° is in the neighborhood of 5500 kg. The compressibility of single crystal arsenic must vary greatly with the direction in the crystal, there being a direction in which the compressibility

is at least 6.7 times greater than the average. The temperature coefficient of resistance at atmospheric pressure between  $0^{\circ}$  and  $100^{\circ}$  is 0.00473. There are several obscure points; why the great hysteresis in the resistance of the high pressure modification, why the difference in the transition pressures from the compressibility and the resistance measurements, and why the positive pressure coefficient of resistance on the virgin specimen, and a nearly constant value of  $-1.5 \times 10^{-6}$  on the same material after it has experienced the transition.

The behavior of arsenic has been previously measured under pressure.<sup>5</sup> The previous specimen was very impure, the temperature coefficient of resistance being only 0.00076. The resistance was found to have a pressure coefficient of  $-3.3 \times 10^{-6}$ . There was considerable irregularity in the previous results, which was not inconsistent with a transition.

*Boron.* The specimen was a rod about 1 cm long and 1.5 mm in diameter. It was most kindly loaned to me for these measurements by Mr. Alfred Loomis of Tuxedo Park, who had obtained it from Dr. G. Holst of Eindhoven. It was prepared by the method developed there by van Arkel of thermal decomposition of the vapor of  $\text{BCl}_3$  and  $\text{BBr}_3$ . It is deposited from the vapor on a core of tungsten wire. The diameter of this wire is of the order of 0.05 mm, making the total impurity of tungsten about 0.1%. Except for this, the material may be expected to be very pure.

The measurements were made with the lever piezometer for short specimens. The shape of the piece of boron was not as regular as would have been desirable; it could not be made to fit the piezometer as well as usual, and the results were much more irregular. Another source of irregularity was the smallness of the effect, because the compressibility of boron is very nearly the same as that of iron. The average departure of a single reading from a smooth curve (which within the limits of error was taken as a straight line) was 6.9% of the maximum measured effect, that is, 6.9% of the difference of compressibility between boron and iron. This means an irregularity of only 0.46% on the actual compressibility, but this is considerably greater than the irregularity usual with other substances. In view of the irregularity in the measurements, no attempt was made to find the temperature coefficient of compressibility, and measurements were made only at  $30^{\circ}$ . The results found for the linear compressibility were:

$$-\Delta l/l_0 = 1.837 \times 10^{-7}p - 0.70 \times 10^{-12}p^2.$$

Assuming equal compressibility in all direction, this gives for the volume compressibility:

$$-\Delta V/V_0 = 5.51 \times 10^{-7}p - 2.2 \times 10^{-12}p^2.$$

The second degree terms in these expressions is contributed entirely by the iron. According to this boron is about 6% less compressible than iron.

The crystal system of boron has not been determined, so that this result does not have as much significance as it might, Richards<sup>7</sup> found for the volume compressibility  $3 \times 10^{-7}$  on a specimen known to be of high impurity. If boron turns out to have cubic symmetry, the entire difference between the result of Richards and myself must be ascribed to difference of purity; if not, part of the difference may well be due to the crystal structure. A value somewhat between 5.5 and 3 would fit into the periodic system of the elements better than either. It seems to me probable that boron will be found to be not of the cubic system and that its volume compressibility will be somewhat less than  $5.5 \times 10^{-7}$ .

*Titanium.* I am indebted for this material to Professor M. A. Hunter, who prepared small coherent slugs of the massive metal by electrolysis of fused salts. The compressibility was measured with the lever piezometer for short specimens. The pieces measured were formed by grinding from the slugs resulting from the electrolysis; two of them were used piled together, of 1.5 and 1.1 cm length. Measurements were made to 12000 kg at 30° and 75°. Within the limits of error, a second degree expression in the pressure reproduces the results. At 30° the average departure of a single reading from a smooth curve was 1.1% of the maximum measured effect, which means 0.3% on the actual compressibility; at 75° the corresponding figures, discarding one reading, were 1.8% and 0.56%.

The crystal system of titanium is known to be hexagonal, with an axial ratio of 1.60. This is very close to the ratio for close packed spheres, so that it is probable that the compressibility of a single crystal of titanium is nearly the same in all directions. Furthermore, the method of preparation of the specimens would not lead to the expectation of any large crystal structure, with any particular direction of orientation preferred. It is therefore probably fairly safe to calculate the volume compressibility from the actual measurements of linear compressibility by assuming equal compressibility in all directions. The results found in this way are:

$$\text{At } 30^{\circ} \quad -\Delta V/V_0 = 7.97 \times 10^{-7}p + 0.12 \times 10^{-12}p^2,$$

$$75^{\circ} \quad -\Delta V/V_0 = 8.68 \times 10^{-7}p - 4.5 \times 10^{-12}p^2.$$

Two features of these results call for comment; the large increase of compressibility with temperature, and the fact that at  $30^{\circ}$  the direction of curvature is abnormal.

Apparently the compressibility of titanium has not been previously measured. The value  $7.97 \times 10^{-7}$  fits in well with its position in the periodic table.

*Manganese.* This material has been already described in connection with measurements of the effect of pressure on resistance. For the compressibility measurements two pieces were ground to the proper shape, of length 0.67 and 0.53 cm; these were then piled together and measured in the lever piezometer for short specimens. Measurements were made at  $30^{\circ}$  and  $75^{\circ}$  to 12000 kg. At  $30^{\circ}$  the average departure of a single reading from a smooth curve was 1.04% of the maximum measured effect, which means 0.27% on the actual compressibility; at  $75^{\circ}$  the corresponding figures were 1.12% and 0.30%. Both the high and low temperature modifications of manganese belong to the cubic system, so that the volume compressibility may be calculated from the linear compressibility assuming equal compressibility in all directions. The following results were found:

$$\text{At } 30^{\circ} \quad -\Delta V/V_0 = 7.91 \times 10^{-7}p - 5.3 \times 10^{-12}p^2,$$

$$75^{\circ} \quad -\Delta V/V_0 = 8.08 \times 10^{-7}p - 4.8 \times 10^{-12}p^2.$$

The only previous value is by Richards,<sup>3</sup> who found  $8.4 \times 10^{-7}$  as the average compressibility up to 500 kg. Both my value and that of Richards is very much out of line with what would be indicated by the neighbors of manganese in the periodic table; this would suggest a value not far from  $5.6 \times 10^{-7}$ .

Potassium Alum.	}	These three alums were made in large single crystals by slow crystallization lasting several weeks from aqueous solution in a room held at constant temperature near $30^{\circ}$ . The material was commercial C. P. The alums are cubic, so that a measurement of the linear compressibility in a single direction is sufficient to determine the cubic compressibility. Potassium alum was the first measured. Under high pressure there was some corrosive action between the alum and the steel parts with which it came in contact. In order to avoid this,
Ammonia Alum.		
Chrome Alum.		

the adjacent steel parts were gold plated. The compressibility of gold is so nearly the same as that of steel that no error can be introduced in this way. All measurements were made with the lever piezometer for short specimens. It was not possible to measure the chrome alum at 75° because of decomposition. The following are the results:

Potassium Alum.		Average Deviation of Single Reading from Smooth Curve.
At 30°	$-\Delta V/V_0 = 63.03 \times 10^{-7}p - 116.1 \times 10^{-12}p^2,$	.15%
At 75°	$-\Delta V/V_0 = 55.74 \times 10^{-7}p - 93.3 \times 10^{-12}p^2.$	.38%
Ammonia Alum.		
At 30°	$-\Delta V/V_0 = 63.54 \times 10^{-7}p - 102.3 \times 10^{-12}p^2,$	.63%
At 75°	$-\Delta V/V_0 = 61.98 \times 10^{-7}p - 100.8 \times 10^{-12}p^2.$	.45%
Chrome Alum.		
At 30°	$-\Delta V/V_0 = 64.86 \times 10^{-7}p - 112.5 \times 10^{-12}p^2.$	.48%

The compressibilities of these three alums are thus nearly the same. The most striking feature in the results is the very pronounced negative temperature coefficient of compressibility of potassium alum. The temperature coefficient of ammonia alum is also negative, but by a smaller amount. There are no previous values of the compressibilities of the alums for comparison.

*Sodium Chlorate.* This material crystallizes in the cubic system, so that a measurement of the linear compressibility in a single direction suffices. The crystal was prepared from the aqueous solution. The solution was maintained in a room at 30° for several weeks, and allowed to evaporate slowly. The source of material was commercial C. P. stock, obtained from a large chemical supply house; the slow crystallization should give a product of high purity. The compressibility sample was 0.61 cm. long, cut from a single crystal.

In the measurement of compressibility it was necessary to use the new piezometer for organic substances in which pressure is transmitted to the substance by mercury, not because  $\text{NaClO}_3$  dissolves in kerosene, but because it combines with it explosively at pressures above 2000 kg, as I had previously found.

Measurements were made to 12000 at 30° and 75°, 14 observations at each temperature. At 30° the average departure of a single reading from a smooth curve was 1.3% of the maximum effect, and

at 75° 1.5%. As already explained, the corrections with this method are much larger than with the lever piezometer; in this case the corrections amounted to 50% of the measured effect. The following are the numerical results, obtained immediately from the measurements, without adjustment:

$$\text{At } 30^\circ \quad - \Delta l/l_0 = 1.765 \times 10^{-6}p - 3.78 \times 10^{-11}p^2,$$

$$\text{At } 75^\circ \quad - \Delta l/l_0 = 1.633 \times 10^{-6}p - 1.92 \times 10^{-11}p^2.$$

The results as given indicate a smaller initial compressibility at 75° than at 30°, which is abnormal, and also a smaller second degree term at 75°, which again is abnormal. The result of the combination of these two factors is that the average compressibility between 0 and 12000 kg is greater at 75° than at 30°, which is normal. A study of the relative magnitude of the errors of a single reading and of the departures from linearity will show that a great deal of significance cannot be attached to the second degree term. The best way to manipulate the results would seem to be to assume that the second degree term is the same at both temperatures and the average of those found, and then to so adjust the initial compressibility that when combined with the second degree term the average compressibility to 12000 kg found experimentally is reproduced at each temperature. In this way the following results were found, making the additional change from linear to volume compressibility. These are to be accepted as the most probable values on the basis of these measurements:

$$\text{At } 30^\circ \quad - \Delta V/V_0 = 4.94 \times 10^{-6}p - 9.3 \times 10^{-11}p^2,$$

$$\text{At } 75^\circ \quad - \Delta V/V_0 = 5.28 \times 10^{-6}p - 9.3 \times 10^{-11}p^2.$$

There seem to be no previous measurements of the compressibility of this substance for comparison.

*Sodium Bromate.* This was grown by slow evaporation from aqueous solution in a constant temperature room over a period of several weeks, like sodium chlorate. The original material was commercial stock, C. P.; the slow crystallization should have been effective in further purification. The sample for the compressibility measurement was cut from a single crystal and was 0.67 cm long. The compressibility was measured in the piezometer for organic substances, submerged under mercury. I did not verify by direct experiment that this spontaneously explodes on contact with kerosene

at high pressures, but used at once the safe method without further inquiry.

Measurements were made to 12000 kg at 30°; a run was also made to 12000 at 75°, but there was evidently something the matter with the measurements, and on taking the apparatus apart, the sodium bromate was found to have completely decomposed, an effect not shown by the chlorate. At 30°, the two points at the lowest pressures lay off the smooth curves by amounts corresponding to about 1000 kg; the remaining points lay on a smooth curve with an average departure of 0.2% of the maximum effect. The dimensions and the magnitude of the effect were somewhat more favorable than in the case of the chlorate, so that the total correction was only 20% of the measured effect.

Sodium bromate is cubic, so that the cubic compressibility can at once be found from the linear compressibility in a single direction. The results were as follows:

$$\text{At } 30^\circ \quad -\Delta V/V_0 = 4.320 \times 10^{-6}p - 7.42 \times 10^{-11}p^2.$$

The compressibility is this somewhat less than that of the chlorate. This is not the direction of difference which one would at first expect, because the atom of bromine is by itself more compressible than the atom of chlorine.

*Sodium Nitrate.* This substance has the same crystal symmetry as calcite, so that the compressibility must be measured in two independent directions, parallel and perpendicular to the axis of trigonal symmetry. The original material was Kahlbaum's purest. It was formed into a single crystal block by my method of slow lowering from the furnace in the molten condition. It was melted in a funnel shaped container of pyrex glass; this has the disadvantage that it sticks on solidifying to the sides of the mold and the resultant block contains many cracks, but in spite of this it was possible to get from the block unfractured pieces large enough, the piece parallel to the trigonal axis being 0.97 cm. long, and that perpendicular to it 0.82 cm. Since sodium nitrate is not soluble in kerosene, the measurements were made in the lever apparatus for short specimens. The measurements on the specimen parallel to the trigonal axis were much more regular than on those perpendicular to it. At 30° the average departure of a single reading from a smooth curve for the perpendicular specimen was 0.9% of the maximum measured effect, and at 75° 0.7%. For the parallel specimen the corresponding figures were 0.1% and 0.4%.

The following are the results for the linear compressibilities. Perpendicular to the trigonal axis:

$$\text{At } 30^\circ \quad -\Delta l/l_0 = 7.093 \times 10^{-7}p - 5.88 \times 10^{-12}p^2,$$

$$\text{At } 75^\circ \quad -\Delta l/l_0 = 7.643 \times 10^{-7}p - 4.41 \times 10^{-12}p^2.$$

Parallel to the trigonal axis:

$$\text{At } 30^\circ \quad -\Delta l/l_0 = 24.36 \times 10^{-7}p - 23.5 \times 10^{-12}p^2,$$

$$\text{At } 75^\circ \quad -\Delta l/l_0 = 23.36 \times 10^{-7}p - 21.4 \times 10^{-12}p^2.$$

From these values of linear compressibility the following may be calculated for the cubic compressibility:

$$\text{At } 30^\circ \quad -\Delta V/V_0 = 38.54 \times 10^{-7}p - 39.2 \times 10^{-12}p^2,$$

$$\text{At } 75^\circ \quad -\Delta V/V_0 = 38.64 \times 10^{-7}p - 35.8 \times 10^{-12}p^2.$$

The compressibility at low pressures at  $0^\circ$  has been found by Madelung und Fuchs<sup>8</sup> to be  $37.7 \times 10^{-7}$ , agreeing fairly well with the initial value of the above formulas.

The compressibility of sodium nitrate has several interesting features. The compressibility in the parallel direction is more than three times as great as in the perpendicular direction. In the perpendicular direction the temperature coefficient of compressibility is positive, as is normal, but the numerical value of the coefficient is much larger than normal. In the parallel direction, the temperature coefficient of compressibility is negative, which is abnormal. Calcite is also three times more compressible parallel to the trigonal axis than at right angles, but the absolute magnitudes are only one-third as large.

*Rochelle Salt.* This belongs to the orthorhombic system, so that observations are necessary in three mutually perpendicular directions. The rods were cut from a single large crystal, which I owe to the kindness of the General Electric Co. It was prepared by the method of slowly lowering the temperature of a saturated aqueous solution. This crystal was prepared at least five years before the measurements were made on it. During these years it has been wrapped in Japanese crepe paper in a tightly closed wooden box; the surface still retained the original glass-like perfection. This material does not dissolve in kerosene, so that measurements were made in the lever apparatus for short specimens. The pressure range was 12000 kg as usual, but it was possible to measure only at  $30^\circ$ , because Rochelle salts

loses its water of crystallization at about  $37^\circ$ , making the usual measurement at  $75^\circ$  impossible.

The designation of the directions used in the following is that usual with crystallographers, for example as that used by Mandel<sup>10</sup> in his recent paper on the elastic constants. The  $a$  and  $b$  directions are at right angles to each other, and lie in the large basal face,  $b$  bisecting the angle of approximately  $80^\circ$ , and  $c$  is perpendicular to both  $a$  and  $b$ . The lengths of the specimens measured were as follows:  $a$ , .73 cm;  $b$ , .91 cm; and  $c$ , 1.17 cm. The measurements in all three directions went rather smoothly; the average departure of a single reading from a smooth curve in terms of the maximum effect was 0.9% for the  $a$  direction, 0.09% for the  $b$  direction, and 0.29% for the  $c$  direction. In each direction the departures from a second degree curve were very large, so that the results must be given in a Table, which follows.

TABLE II.  
COMPRESSIBILITY OF ROCHELLE SALT AT  $30^\circ$ .

Pressure kg/cm <sup>2</sup>	$-\Delta l/l_0$			$-\Delta V/V_0$
	$a$	$b$	$c$	
2000	.00245	.00506	.00333	.01080
4000	.00460	.00969	.00600	.02016
6000	.00651	.01414	.00847	.02885
8000	.00843	.01833	.01085	.03716
10000	.01029	.02217	.01320	.04501
12000	.01209	.02586	.01531	.05237

The cubic compressibility of Rochelle salts has not been previously measured, but all of the elastic moduli have been measured by Mandel, from which the linear compressibilities can at once be calculated. Mandel's<sup>9</sup> values for the moduli in Abs. C. G. S. units are:

$$s_{11} = 46.0 \times 10^{-10},$$

$$s_{22} = 31.4 \times 10^{-10},$$

$$s_{33} = 27.6 \times 10^{-10},$$

$$s_{44} = 59.7 \times 10^{-10},$$

$$s_{55} = 300.4 \times 10^{-10},$$

$$s_{66} = 78.7 \times 10^{-10},$$

$$s_{23} = 16.5 \times 10^{-10},$$

$$s_{31} = -21.4 \times 10^{-10},$$

$$s_{12} = -7.8 \times 10^{-10}.$$

From these the linear compressibilities in kg units may be calculated to be:

Linear compressibility in *a* direction ( $= s_{11} + s_{12} + s_{13}$ )  $= 16.8 \times 10^{-7}$ ,

Linear compressibility in *b* direction ( $= s_{12} + s_{22} + s_{23}$ )  $= 40.1 \times 10^{-7}$ ,

Linear compressibility in *c* direction ( $= s_{13} + s_{23} + s_{33}$ )  $= 22.7 \times 10^{-7}$ .

By drawing smooth curves through the points given in the table and taking the tangent at the origin, the corresponding initial compressibilities given by my data are: 13.3, 27.1, and  $19.5 \times 10^{-7}$ . These are all considerably lower than the values of Mandel, and the difference is much too great to be explained by mere errors of observation. The difference must be ascribed to difference in the original material; it is well known that the electrical properties of Rochelle salt crystals may be very greatly altered by various processes of seasoning or dessication, and there is no reason not to expect corresponding variability in the elastic properties. The most natural explanation of the difference is difference of water content. It will be seen that the ratio of my compressibilities in different directions is not the same as that of Mandel; this means that different degrees of dessication affect the properties differently in different directions.

*Ammonium Tartrate.* The C. P. material of commerce occurs in large enough single crystals so that suitable pieces were found by selection. This material is monoclinic, so that, strictly, linear compressibility measurements are necessary in four directions to completely fix the behavior under pressure. However, the *a* axis, using the usual designation of the axes as given, for example, in Groth, is so nearly at right angles to *b* and *c* that the measurement in a fourth direction, exactly perpendicular to *b* and *c*, was dispensed with.

This material is not soluble in kerosene, so that the compressibility was measured in the lever piezometer for short specimens. The lengths of the specimens were as follows: *a*, 0.48 cm; *b*, 0.87 cm; and *c*, 1.00 cm. Readings were made to 12000 kg at both 30° and 75°. The departure of a single reading from a smooth curve in terms of the maximum effect was: *a* direction, 1.2% at 30° and 1.4% at 75°; *b* direction, 0.3% at 30° and 0.2% at 75°; *c* direction, 0.16% at 30° and 0.34% at 75°.

Within the limits of error the relation between change of length and pressure can be represented by a second degree curve in the pressure. The results follow:

*a* direction

$$\text{At } 30^\circ \quad -\Delta l/l_0 = 8.47 \times 10^{-7}p - 16.8 \times 10^{-12}p^2,$$

$$\text{At } 75^\circ \quad -\Delta l/l_0 = 8.75 \times 10^{-7}p - 19.3 \times 10^{-12}p^2.$$

*b* direction

$$\text{At } 30^\circ \quad -\Delta l/l_0 = 13.71 \times 10^{-7}p - 9.3 \times 10^{-12}p^2,$$

$$\text{At } 75^\circ \quad -\Delta l/l_0 = 14.51 \times 10^{-7}p - 11.8 \times 10^{-12}p^2.$$

*c* direction

$$\text{At } 30^\circ \quad -\Delta l/l_0 = 26.85 \times 10^{-7}p - 46.1 \times 10^{-12}p^2,$$

$$\text{At } 75^\circ \quad -\Delta l/l_0 = 27.48 \times 10^{-7}p - 48.2 \times 10^{-12}p^2.$$

## Approximate volume compressibility:

$$\text{At } 30^\circ \quad -\Delta V/V_0 = 49.03 \times 10^{-7}p - 79.3 \times 10^{-12}p^2,$$

$$\text{At } 75^\circ \quad -\Delta V/V_0 = 50.84 \times 10^{-7}p - 87.0 \times 10^{-12}p^2.$$

Again we find a compressibility in one direction about three times as great as in another. The behavior of the compressibility with temperature and the second degree terms offer no unusual features.

*Tartaric Acid.* This was prepared by slow evaporation in the constant temperature room from aqueous solution of commercial C. P. material. The crystal is monoclinic; the *a* axis is inclined at  $80^\circ$  to the plane of *b* and *c*, and as in the case of ammonium tartrate the compressibility was determined only along the three crystallographic axes. The lengths of the specimens in the *a*, *b*, and *c* directions were respectively: 0.77, 0.62, and 0.67 cm. This material is also not soluble in kerosene, and the measurements were made in the lever apparatus for short specimens. Measurements were made to 12000 kg at  $30^\circ$  and  $75^\circ$ . In the *c* direction an unusual seasoning effect was found, the points obtained with increasing pressure being irregular and lying far off the descending curve, which by every appearance was the correct curve. Discarding the ascending points of the *c* direction, the average departures of a single reading from a smooth curve at  $30^\circ$  and  $75^\circ$  were respectively: *a* direction, 0.5% and 0.9%; *b* direction, 0.1% and 0.02%; *c* direction, 0.5% and 0.13%.

The results can be reproduced by a second degree expression in the pressure, and are as follows:

*a* direction

$$\text{At } 30^\circ \quad -\Delta l/l_0 = 8.19 \times 10^{-7}p - 11.7 \times 10^{-12}p^2,$$

$$\text{At } 75^\circ \quad -\Delta l/l_0 = 8.26 \times 10^{-7}p - 13.8 \times 10^{-12}p^2.$$

*b* direction

$$\text{At } 30^\circ \quad -\Delta l/l_0 = 50.78 \times 10^{-7}p - 110. \times 10^{-12}p^2,$$

$$\text{At } 75^\circ \quad -\Delta l/l_0 = 53.63 \times 10^{-7}p - 126. \times 10^{-12}p^2.$$

*c* direction

$$\text{At } 30^\circ \quad -\Delta l/l_0 = 10.89 \times 10^{-7}p - 16.0 \times 10^{-12}p^2,$$

$$\text{At } 75^\circ \quad -\Delta l/l_0 = 13.73 \times 10^{-7}p - 33.1 \times 10^{-12}p^2.$$

Approximate volume compressibility, obtained by treating these three directions as if perpendicular:

$$\text{At } 30^\circ \quad -\Delta V/V_0 = 69.86 \times 10^{-7}p - 148 \times 10^{-12}p^2,$$

$$\text{At } 75^\circ \quad -\Delta V/V_0 = 75.62 \times 10^{-7}p - 186 \times 10^{-12}p^2.$$

The temperature coefficient of compressibility in the *b* and *c* directions has the normal sign, but is abnormally large. There is no simple connection between the compressibility of tartaric acid and of ammonium tartrate, the roles of the *b* and the *c* axes being reversed.

*Diphenylamine.* The origin of this was chemically pure material from Kahlbaum. It was made into large single crystals from the melt in a thermostat. This ordinarily crystallizes in thin plates, but by holding at the melting temperature for several days the plates were induced to grow to about 3.8 mm thickness, sufficient to give the compressibility perpendicular to the face of the plate, the *c* direction, by piling together two pieces. This material is monoclinic but again the three axes are nearly at right angles, and the linear compressibility was determined only in the direction of the axes. The designation of the axes is that of Groth, the *a* and *b* axes being in the flat face, at right angles, and the *c* axis perpendicular to both.

Diphenylamine is soluble in kerosene, so that it was necessary to use the piezometer for organic substances, submerging the crystal beneath mercury. Measurements were made to 12000 kg at  $30^\circ$ ; the melting point is at about  $54^\circ$ , so that the customary measurements at  $75^\circ$  could not be made. In the *c* direction the points at 11000 and 12000 lay off the curve, there being evidently some sort of interference with the free motion of the slide wire. With the exception of these two points, the average deviation of a single reading from a smooth curve, in terms of the maximum effect, was 1.1% for the *a* direction, 1.2% for the *b* direction, and 0.4% for the *c* direction. The corrections were not as large a fraction of the total effect as is

sometimes the case, being 8% in the *a* direction, 8% in the *b* direction, and 10% in the *c* direction. The lengths of the *a* and the *b* specimens were 0.8 cm.

The relation between change of dimensions and pressure is distinctly not of the second degree, so that the results are best exhibited in the following table:

TABLE III.  
COMPRESSIBILITY OF DIPHENYLAMINE AT 30°.

Pressure kg/cm <sup>2</sup>	<i>a</i>	$-\Delta l/l_0$ <i>b</i>	<i>c</i>	$-\Delta V/V_0$
3000	.0147	.0145	.0164	.0463
6000	.0259	.0256	.0266	.0802
9000	.0358	.0353	.0332	.1079
12000	.0442	.0435	.0383	.1313

The compressibility is very much more nearly equal in the three directions than is usually the case for crystals. This means that the change of volume can be calculated with very little error from the linear changes. The volume compressibility is high for a solid, and is almost exactly the same as for liquid glycerine, the least compressible organic liquid yet measured.

( $NH_2C_6H_5$ )<sub>2</sub>SnCl<sub>6</sub>. This material I owe to the kindness of Dr. R. W. G. Wyckoff of the Rockefeller Institute for Medical Research. Particular interest attaches to it because it is one of the few organic substances which crystallize in the trigonal system, and because its X-ray structure has been completely worked out.<sup>10</sup> The substance crystallizes in the form of hexagonal plates; two plates were available of a thickness of 0.16 and 0.12 cm. Two determinations of compressibility are necessary, one parallel to the hexagonal face and one perpendicular to it. The parallel specimen had a length of 0.65 cm. The perpendicular measurements were made on pieces cut from the two plates, piled together. The measurements had to be made in the piezometer for organic substances, submerged under mercury, for the double reason that it is dissolved by kerosene and it is too soft mechanically to withstand the necessary compression in the lever apparatus. The specimens were prepared by shaving off the excess material with a razor blade. It was not possible in this way to make as perfect specimens as by grinding, and the results are much more irregular than usual, both because of the geometrical imperfection of the specimens and because of their small size.

No attempt was made to measure the compressibility at 75°. The accuracy was not great enough to give departures from linearity. With the parallel specimen the average departure of a single reading from a straight line was 5% of the maximum effect. With the perpendicular specimen, there was some sort of permanent change produced by the pressure, and the points with increasing and decreasing pressure lay on two different lines of approximately the same slope, the average departure of a single reading from one or the other of these lines being about 1.5%. The material is affected in some way by its contact with kerosene under pressure, its mechanical texture becoming more friable, and the appearance being almost as if it had been amalgamated, although retaining its original shape. The corrections were about 5% of the measured effect. The results follow:

30°, average to 12000 kg/cm<sup>2</sup>,

- $\Delta l/l_0 = 3.95 \times 10^{-6}p$ , parallel to hexagonal face,
- $\Delta l/l_0 = 5.75 \times 10^{-6}p$ , perpendicular to hexagonal face,
- $\Delta V/V_0 = 12.9 \times 10^{-6}p$ .

The volume compressibility is thus sensibly greater than that of diphenylamine, and is the largest yet measured in a crystalline solid. The difference of compressibility in the two directions is not as great as might be expected.

*Bakelite.* The new piezometer for organic substances was first checked as to its proper functioning by measuring with it the compressibility of bakelite. Although this is not a chemically well defined substance, it is used to some extent in the construction of instruments, and the results found are therefore tabulated as being of some practical interest. The material investigated was the clear light yellow material, in appearance like amber. The relation between pressure and change of length is not of the second degree. The following are the results, the change of volume being calculated on the assumption of equal compressibility in all directions. Meas-

TABLE IV.

COMPRESSIBILITY OF BAKELITE AT 30°.

Pressure kg/cm <sup>2</sup>	— $\Delta l/l_0$	— $\Delta V/V_0$
4000	.0250	.073
8000	.0437	.125
12000	.0577	.163

urements were made only at 30°. The compressibility is seen to be high, getting up into the class of organic liquids.

#### DISCUSSION AND SUMMARY.

The effect of pressure on the electrical resistance of four metallic elements is measured. The resistance decreases with rising pressure in all cases, as is normal, with the exception of an initial effect found in arsenic. The compressibility of four elements, seven inorganic single crystals, four organic crystals, and bakelite is measured. A new form of piezometer has been developed for those substances which dissolve in kerosene. Arsenic has a new polymorphic form at high pressures, the transition pressure at 30° being about 5500 kg/cm<sup>2</sup>. The compressibility differences of single crystal arsenic in different directions are very large. The compressibility measurements make it probable that boron does not crystallize in the cubic system. The organic crystals in general do not show as large compressibility differences in different directions as inorganic crystals. The absolute compressibility of the organic solids is high, the volume decrease under 12000 kg/cm<sup>2</sup> being of the order of 15%.

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